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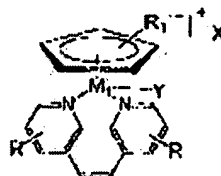
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(54) METHOD FOR PRODUCING FORMIC ACID FROM CARBON DIOXIDE AND HYDROGEN AND METHOD FOR FIXING CARBON DIOXIDE AND METHOD FOR ACCELERATING THE REACTIONS BY IRRADIATION OF LIGHT

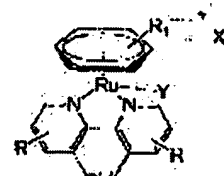
(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing formic acid, comprising reacting carbon dioxide with hydrogen in the presence of a compound useful as a catalyst for reacting the carbon dioxide with hydrogen, and to provide a method for fixing the carbon dioxide.

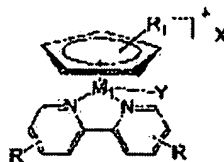
SOLUTION: This method for producing the formic acid comprises reacting carbon dioxide with hydrogen in the presence of one of compounds represented by general formulas (I) to (IV) [R1 groups are each identically or differently H, an alkyl, an aromatic group, OH, COOR, CONRR', halogen (X), OR, SR, NRR', or PRR'R"; M1 groups are each identically or differently Ir, Rh or Ru; R is H, an alkyl, an aromatic group, OH, COOR, CONRR',



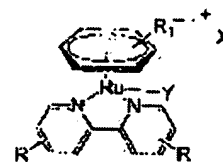
(I)



(II)



(III)



(IV)

X, OR, SR, or the like; Y is a halogen or H; X is a counter anion for forming a metal complex], and the method for fixing the carbon dioxide comprises utilizing the above-described reaction.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which this invention belongs]

This invention relates to the approach of promoting them, by making the manufacture approach of the formic acid to which a carbon dioxide and hydrogen are made to react, the fixed approach of a carbon dioxide, and light irradiate.

[0002]

[Description of the Prior Art]

From the former, the very thing was known for making a carbon dioxide and hydrogen react. For example, as a reaction, it is Chem. conventionally. Lett. p.863 (1976) Chem. Commun. p. 1465 (1993) Although JP,51-138614,A, JP,56-166146,A, etc. are mentioned, additives, such as an amine, are required in each using an organic solvent for these reactions. (Patent reference 1, patent reference 2, and nonpatent literature 1 reference)

Moreover, it is JP,7-173098,A and JP,2001-288137,A to make it react in supercritical, An organic combination chemistry association magazine, volume [52nd] No. 12 pp.1032-1043 (1994), Nature Vol 368 and p. 231 (1994) Chem. Lett. p.1016 (2001) J. Am. Chem. Soc. p. 7963 (2002) J. Am. Chem. Soc. p. 344 (1996) Inorg.Chem. p. 1606 (2002) etc. -- it is indicated. (Two to patent reference 3-4 and nonpatent literature 7 reference)

Furthermore, it is JP,56-140948,A to make it react in a water solution. Chem. Commun. p.971 (1999) Appl. Organometal. Chem. p 857 (2000) Inorg. Chem. p. 5083 (2000) It is indicated. (Eight to patent reference 5 and nonpatent literature 10 reference)

Reaction in an ordinary temperature ordinary pressure sewage solution using the solid-state catalyst further again J. Am. Chem. Soc. p.6319 (1983) In addition to this, many catalytic hydrogenation reactions of the carbon dioxide using a solid-state catalyst are known. (Nonpatent literature 11 reference)

Moreover, most was having the Lynn ligand used [catalyst / of the catalytic hydrogenation reaction of the carbon dioxide known until now / homogeneous system metal complex], and there were few things using a nitrogen ligand until now. (Nonpatent literature 12 and nonpatent literature 13 reference)

On the other hand, the hydrogenation reaction of a carbon dioxide was not known until now, making light irradiate. The reduction reaction of the carbon dioxide by light is Helv. Chim. Acta p. 1065 (1986) Although known for many years, it was a reaction in an organic solvent, and sacrifice reagents, such as an amine, were indispensable, and the reaction rate was very slow, and the complicatedness of isolation purification of a product etc. was not [like] fit for utilization. (Nonpatent literature 14 reference)

[Patent reference 1] JP,51-138614,A

[Patent reference 2] JP,56-166146,A

[Patent reference 3] JP,7-173098,A

[Patent reference 4] JP,2001-288137,A

[Patent reference 5] JP,56-140948,A official report

[Nonpatent literature 1] Chem. Lett. p.863 (1976) Chem. Commun. p. 1465 (1993)

[Nonpatent literature 2] Organic combination chemistry association magazine, volume [52nd] No. 12 pp.1032-1043 (1994)

[Nonpatent literature 3] Nature Vol 368, p. 231 (1994)

[Nonpatent literature 4] Chem. Lett. p.1016 (2001)

[Nonpatent literature 5] J. Am. Chem. Soc. p. 7963 (2002)

[Nonpatent literature 6] J. Am. Chem. Soc. p. 344 (1996)

[Nonpatent literature 7] Inorg.Chem. p. 1606 (2002)

[Nonpatent literature 8] Chem. Commun. p. 971 (1999)

[Nonpatent literature 9] Appl. Organometal. Chem. p 857 (2000)

[Nonpatent literature 10] Inorg. Chem. p. 5083 (2000)

[Nonpatent literature 11] J. Am. Chem. Soc. p.6319 (1983)

[Nonpatent literature 12] J. Mol. Cata. A 1995, v. 101, p. 33

[Nonpatent literature 13] J. Mol. Cata. 1989, v. 57, p. 47

[Nonpatent literature 14] Helv. Chim. Acta 1986, v. 69, p. 1065

[0003]

[Problem(s) to be Solved by the Invention]

The concentration in the atmospheric air of a carbon dioxide is increasing every year, and development of the fixing method is a urgent technical problem. Although he thinks that it is discarded for the time being to the underground all over the sea, as many parts as possible [prospective] can be reused as a carbon resource, and chemistry conversion to the organic compound of a liquid with easy storage or a solid-state is desired. moreover, energy expenditure from which generating of a new carbon dioxide is suppressed at the process -- development of few transformation methods is indispensable.

in recent years, effective in chemical immobilization of the carbon dioxide by the hydrogenation reaction -- high -- development of an activity transition metal complex catalyst is desired.

Until now, mainly generating a formic acid or its derivative is known by the hydrogenation reaction of the carbon dioxide using a transition metal complex. if a typical example is given -- (1) Chem. Lett. p.863 (1976) etc. -- approach of manufacturing a formic acid under existence of organic amines, such as triethylamine, among an organic solvent or a mixed solvent with water like. (2) The approach to which the carbon dioxide in a supercritical condition and hydrogen are made to react under alkali existence, such as an amine, in JP,7-173098,A. (3) JP,56-140948,A, Chem. Commun. p. 971 (1999) How to manufacture a formic acid from the carbon dioxide in a water solution and hydrogen of the indicated carbonate. (4) J. Am. Chem. Soc. p.6319 (1983) making hydrogen lead by the ordinary temperature ordinary pressure in a water solution of the carbonate using the indicated support palladium -- the method of manufacturing a formic acid etc. is learned. (1) About -(3), it is J. Am. Chem. Soc. p. 7963 (2001) It is collected.

By the approach of of the above (1) and (2), it being necessary to add the organic substance, such as an amine and alcohol, and and the amount of a formic acid to generate have problems, such as separation of being restricted to a maximum of 2 about times of additions, such as an amine, the formic acid which is a product further, and the added organic substance. The approach of of (3) and (4) is a reaction in a water medium, and it has the description of not using the organic substance, and although especially (4) is an ordinary pressure reaction or a reaction in low voltage, it cannot be said to be enough [all / a catalyst rotational frequency or catalyst rotation effectiveness], and is not suitable for practical use. Although catalyst effectiveness of (2) is high compared with other approaches, it is necessary to generate a supercritical condition and a high-pressure reaction system and complicated actuation are needed.

On the other hand, in the hydrogenation reaction of an old carbon dioxide, the driving force of formic-acid generation was what is depended on a pressure or heat. It is very meaningful that light energy can be used instead of a pressure or heat. The photoreduction reaction of the carbon dioxide known conventionally was a reaction in an organic solvent, its sacrifice reagents, such as an amine, were indispensable, and its reaction rate was very slow, and the complicatedness of isolation generation of a

product etc. was not fit for utilization.

The technical problem which this invention tends to solve is offering the method of fixing the carbon dioxide led to a formic acid by hydrogenation of a carbon dioxide by irradiating mild conditions or light under transition metal complex catalyst existence among the water medium which does not use the organic substance at all.

[0004]

[Means for Solving the Problem]

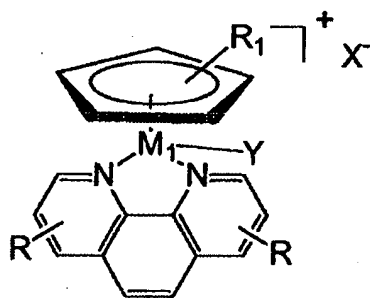
This invention is characterized by a carbon dioxide hydrogenating under a mild condition under the catalyst existence of the compound of metal complexes, such as iridium, a rhodium, and a ruthenium, among the water solution which does not use the organic substance at all, irradiating the light depending on the case.

This invention is being able to check the hydrogenation reaction of a carbon dioxide occurring and offering the method of fixing a carbon dioxide using the manufacture approach of formic acid, and this reaction, while the new metal complex which has a specific organic-nitrogen-compounds ligand irradiates the light among water and the water solution of mineral salt depending on the case, as a result of performing retrieval of a catalyst, and examination of the system of reaction, in order to make the reaction of a carbon dioxide and hydrogen perform.

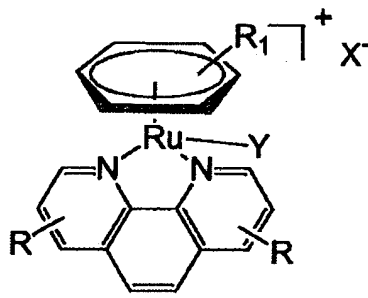
namely

It faces making a carbon dioxide and hydrogen react, and they are water, a general formula (I) - (IV).

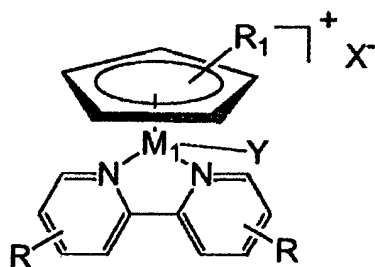
[Formula 3]



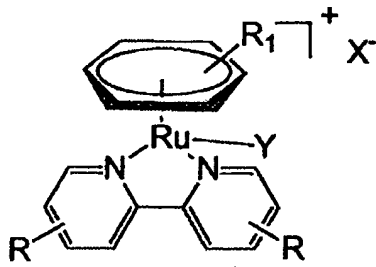
(I)



(II)



(III)



(IV)

(Among a formula, R1 is hydrogen atom, alkyl group, aromatic series radical, hydroxyl-group (-OH), and ester group (-COOR), amide group (-CONRR'), a halogen (-X), an oxygen functional group (-OR), a sulfur functional group (-SR), a nitrogen functional group (-NRR'), and the Lynn functional group (-

PRR'R"), may be the same or may differ.) M1 is Ir, Rh, or Ru, and R is a hydrogen atom, an alkyl group, an aromatic series radical, a hydroxyl group (-OH), and an ester group (-COOR). It is amide group (-CONRR'), a halogen (-X), an oxygen functional group (-OR), a sulfur functional group (-SR), a nitrogen functional group (-NRR'), and the Lynn functional group (-PRR'R"), and it may be the same or you may differ. Y is a halogen or hydrogen and X expresses the counter anion which forms a metal complex. Under existence of one which is expressed of compounds, the method of fixing a carbon dioxide was able to be offered using the manufacture approach of the formic acid to which a carbon dioxide and hydrogen are made to react, and this reaction.

[0005]

[Embodiment of the Invention]

The iridium indicated to be the "complex" used in this invention by the general formula (I) - (IV), a rhodium, and a ruthenium metal complex catalyst are used.

the cyclopentadienyl ligand and arene ligand of a metal complex which are used by this invention -- an aliphatic series (alkyl group) radical, an alicycle group machine, an aromatic series radical, an ester group (-CO₂R), an amide group (-CONRR'), a halogen (-X), an oxygen functional group (-OR), a sulfur functional group (-SR), a nitrogen functional group (-NRR'), the Lynn functional group (-PRR'R"), etc. -- one piece -- or more than one may be permuted. When permuting more than one, it does not matter even if the same and it differs. Especially, on a rhodium and iridium, the activity of a hexamethylbenzene ligand is high to a pentamethylcyclopentadienyl ligand and a ruthenium.

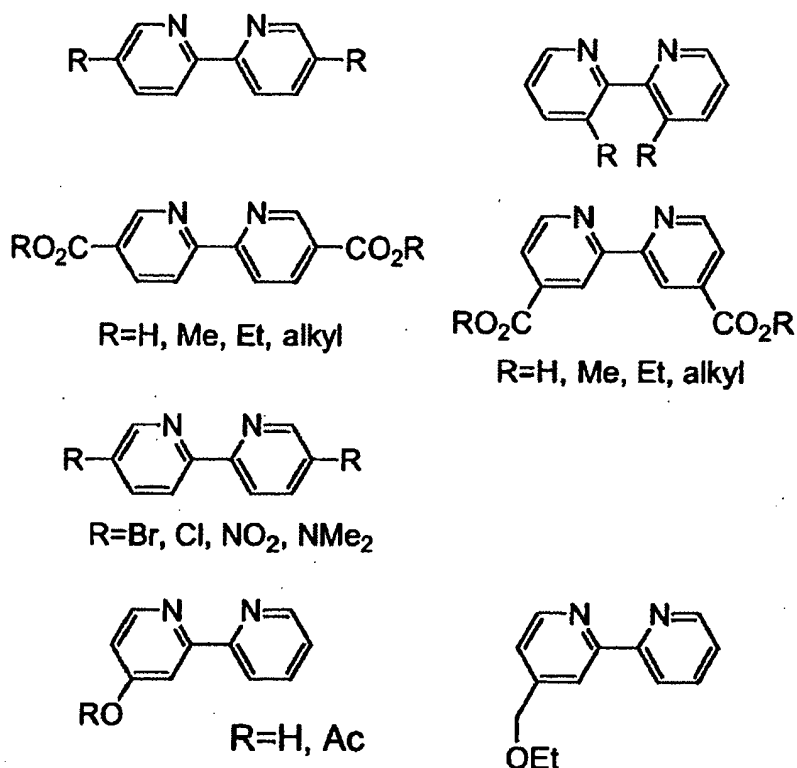
An organic-nitrogen-compounds ligand is used for the metal complex used by this invention. Especially a bipyridine or a phenanthroline derivative is desirable. R in a formula is a hydrogen atom, an alkyl group, an aromatic series radical, a hydroxyl group (-OH), and an ester group (-COOR). Substituents, such as amide group (-CONRR'), a halogen (-X), an oxygen functional group (-OR), a sulfur functional group (-SR), a nitrogen functional group (-NRR'), and the Lynn functional group (-PRR'R"), are shown. Moreover, the same or a different substituent is sufficient as R. As long as the ligand combined with the metal atom of the metal complex used by this invention can form the bottom hydride complex (Y=H) of hydrogen content child existence, what kind of thing is sufficient as it. For example, halogen ion, an AKUA ligand (H₂O), etc. are mentioned. Here, a hydride complex (Y=H) functions as a catalyst of this reaction.

Especially the counter anion of the metal complex used by this invention does not limit the class. For example, as long as it dissolves a halogen anion, a perchloric acid anion, etc. in reaction mixture, what kind of thing may be used.

[0006]

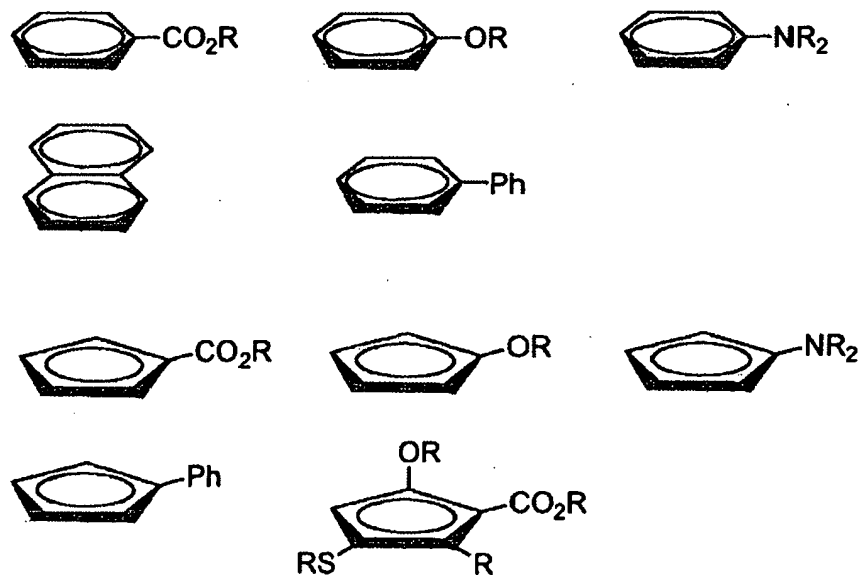
There is the following as an example of the poly pyridine ligand used with the metal complex used by this invention.

[Formula 4]



Moreover, there is the following as an example of the cyclopentadienyl ligand used with the metal complex used by this invention, and an arene ligand. (In the following type, R is hydrogen or an alkyl group, may be the same or may differ.)

[Formula 5]



Water is used as a medium used by this invention. A reaction advances in pure water or the water solution of mineral salt. Preferably, the mineral salt which presents the alkalinity in a water solution is

desirable. especially -- the [the Ith group or] -- II group's carbonate or hydrogencarbonate -- desirable -- as the example -- Li_2CO_3 LiHCO_3 Na_2CO_3 NaHCO_3 K_2CO_3 KHCO_3 CaCO_3 BaCO_3 SrCO_3 etc. is mentioned. the [or / the Ith group who generates a carbonate or a hydrogencarbonate for a carbon dioxide press fit or by carrying out bubbling, or] -- II group's hydroxide -- desirable -- as the example -- LiOH NaOH KOH calcium $(\text{OH})_2$ $\text{Ba}(\text{OH})_2$ $\text{Sr}(\text{OH})_2$ etc. is suitable. Moreover, even if it mixes the organic substance, such as alcohol and an amine, in order not to bar a reaction at all, the mixed solvent of the water-organic substance may be used.

About the amount of the above-mentioned metal complex used in this invention, there are not an upper limit and a minimum and they are dependent on the solubility to reaction mixture, economical efficiency, etc. Suitable catalyst concentration is 1×10^{-8} to 1×10^{-3} . It is M and is 1×10^{-7} to 1×10^{-4} preferably. It is referred to as M.

Although the pressure used for the reaction in this invention does not have especially an upper limit and a minimum, generally more than ordinary pressure is used. Although the higher one of a pressure is desirable, it is dependent on the economical reasons of equipment, operation cost, etc.

It is more advantageous for a reaction to advance with reaction rate with the sufficient reaction temperature in this invention. 40 degrees [200 or less] or more are preferably desirable.

Although the light source in this invention used the xenon lamp (light which cut the wavelength below 400 nm and more than 750 nm) of 500W, sunlight is sufficient as it.

[0007]

A reaction will be promoted if it is performed the fixed approach of the carbon dioxide to which the manufacture approach and the carbon dioxide, and hydrogen of formic acid of this invention are made to react irradiating light.

Moreover, it is checked that there is effectiveness in an interesting thing also by ultraviolet rays and the visible ray except infrared radiation.

[0008]

Examples 1-14

content volume 20 ml the water solution (10 ml) of the mineral salt fully deaerated with the predetermined metal complex to the autoclave -- teaching -- the mixed gas of 1 to 1 of a carbon dioxide and hydrogen gas -- a predetermined pressure -- press fit -- or bubbling was carried out and it reacted by predetermined temperature and time amount. Liquid chromatography performed analysis of the generated formic acid. That is, some resultants are extracted and it is this 2 It is wavelength 210 about through and the liquid flowing out to the column (TSKgel SCX(H⁺):TOSOH) which uses mM phosphoric-acid water solution as a developing solution. The absorbance in nm was measured and was computed from the measured value and the calibration curve which were acquired. The result was shown in Table 1.

[0009]

[Table 1]

表1 Rh, Ru, Ir錯体を用いた二酸化炭素の水素化

実施例	触媒 / 濃度	反応条件		触媒回転数	触媒回転効率 ^a	最終辛酸濃度 / mM
		反応溶液 / 反応時間 (h) / 温度(°C)	触媒			
1	Cp*Rh(bpy)Cl ₂ / 1x10 ⁻⁴	1 N KOH / 60 / 80		360	5.8	36
2	Cp*Rh(bpy)Cl ₂ / 1x10 ⁻⁴	H ₂ O / 20 / 40		97	4.9	20
3	Cp*Rh(bpy)Cl ₂ / 1x10 ⁻⁴	フタル酸標準液 (pH 4.01) / 20 / 40		97	4.9	20
4	Cp*RhL ¹ Cl ₂ / 1x10 ⁻⁴	1 N KOH / 60 / 80		320	5.3	32
5	Cp*RhL ¹ Cl ₂ / 1x10 ⁻⁴	0.2 M NaH ₂ PO ₄ / 20 / 80		50	2.5	5
6	Cp*RhL ² Cl ₂ / 1x10 ⁻⁴	1 N KOH / 60 / 80		360	5.8	36
7	Cp*RhL ² Cl ₂ / 1x10 ⁻⁴	H ₂ O / 20 / 80		110	5.5	11
8	Cp*RhL ³ Cl ₂ / 1x10 ⁻⁴	0.2 M NaH ₂ PO ₄ / 20 / 80		124	6.2	12
9	Cp*Rh(phen)Cl ₂ / 1x10 ⁻⁴	1 N KOH / 20 / 80		216	11	22
10	Cp*Rh(phen)Cl ₂ / 1x10 ⁻⁴	H ₂ O / 20 / 80		130	6.5	13
11	Cp*RhL ³ Cl ₂ / 1x10 ⁻⁴	1 N KHCO ₃ / 21 / 80		2400	114	240
12	(C ₆ Me ₆)Ru(phen)Cl ₂ / 1x10 ⁻⁴	1 N KOH / 60 / 80		50	0.8	5
13	Cp*Ir(phen)Cl ₂ / 1x10 ⁻⁴	1 N KOH / 20 / 80		58	3	6
14	Cp*IrL ³ Cl ₂ / 1x10 ⁻⁴	1 N KOH / 19 / 80		5400	242	540

Cp*=pentamethylcyclopentadienyl, bpy=2,2'-bipyridine, phen=1,10-phenanthroline

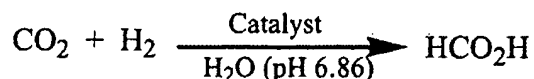
L¹=2,2'-bipyridine-4,4'-dicarboxylic acid, L²=4,4'-dimethyl-2,2'-bipyridine, L³=4,7-dihydroxy-1,10-phenanthroline.反応条件: p = 4 MPa (CO₂:H₂ ≈ 1:1);^a反応1時間当たりの触媒回転数

Examples 15-20

Content volume 20 ml ph fully deaerated with the predetermined metal complex (10micromol) to the stainless steel autoclave and the autoclave made from glass, respectively The phosphoric-acid buffer solution (10 ml) of 6.86 was prepared, and the mixed gas of 1 to 1 of a carbon dioxide and hydrogen gas was pressed fit by 4MPa(s). The autoclave made from glass was irradiated with the xenon lamp (light which cut the wavelength below 400 nm and more than 750 nm) of 500W. Churning was performed for these equipments at the room temperature for 20 hours. Liquid chromatography performed analysis of the generated formic acid, and the result was shown in Table 2.

[Table 2]

表2 可視光で活性化される二酸化炭素の水素化反応



実施例	触媒	触媒回転数 (光照射)	触媒回転数 (暗反応)
15	$\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}_2$	66	3
16	$\text{Cp}^*\text{Ir}(\text{Phen})\text{Cl}_2$	41	< 1
17	$\text{Cp}^*\text{IrL}^1\text{Cl}_2$	59	2
18	$\text{Cp}^*\text{IrL}^2\text{Cl}_2$	47	< 1
19	$\text{Cp}^*\text{IrL}^3\text{Cl}_2$	37	2
20	$\text{Cp}^*\text{IrL}^4\text{Cl}_2$	12	< 1

Cp^* =pentamethylcyclopentadienyl, bpy=2,2'-bipyridine, phen=1,10-phenanthroline

L^1 =5,5'-dimethyl-2,2'-bipyridine, L^2 =2,2'-bipyridine-4,4'-dicarboxylic acid,

L^3 =2,2'-bipyridine-5,5'-dicarboxylic acid, L^4 =4,7-diphenyl-1,10-phenanthroline.

反応条件 : $c(\text{catalyst}) = 1 \text{ mM}$; $p = 4 \text{ MPa}$ ($\text{CO}_2:\text{H}_2 \approx 1 : 1$); $t = 25^\circ\text{C}$; $T = 20 \text{ h}$;
in pH 6.86 phosphate buffer solution

[0010]

As shown in Table 1, when the carbon dioxide was hydrogenated by the water medium about the metal complex catalyst shown by the general formula (I) - (IV), it found out that a formic acid generated. At the reaction using this poly pyridine system ligand, a reaction advances also under the neutrality which was not known and acid conditions not only in the bottom of a basic condition but in a conventional method (examples 2, 3, 5, 7, 8, and 10). Moreover, the ruthenium and the iridium complex were also found by having catalytic activity similarly (example 12-14). It turned out that especially the catalytic activity of the complex which has the ligand which has a hydroxy group on a pyridine ring improves by leaps and bounds (examples 11 and 14).

Table 2 showed the facilitatory effect of the hydrogenation reaction of the carbon dioxide by the light. A reaction is promoted by irradiating the light with a room temperature, in the example 15-20, although a dark reaction hardly advances so that clearly.

[0011]

[Effect of the Invention]

According to this invention, the manufacture approach of the formic acid to which a carbon dioxide and hydrogen are made to react, and the fixed approach of a carbon dioxide were able to be offered using the catalyst to which a carbon dioxide and hydrogen are made to react as stated above. The descriptions of this invention are low voltage conditions comparatively compared with the method of hydrogenating an old carbon dioxide, and do not need the organic substance, such as an amine, but it has the description with which a reaction advances also under neutrality or acid conditions besides basic conditions.

Moreover, in this reaction, the photoactivation effectiveness of a catalyst is shown and it becomes the first example at the hydrogenation reaction of a carbon dioxide. As driving force of a hydrogenation

reaction, it can become technique very effective in carbon-dioxide reduction that light energy can be used in addition to a pressure or heat.

[Translation done.]